
(12) UK Patent Application (19) GB (11) 2 120 695 A

(21) Application No **8310065**
 (22) Date of filing **14 Apr 1983**
 (30) Priority data
 (31) **368736**
 (32) **15 Apr 1982**
 (31) **411295**
 (32) **25 Aug 1982**
 (33) **United States of America (US)**
 (43) Application published
7 Dec 1983
 (51) INT CL³
D06P 1/06
 (52) Domestic classification
D1P 1110 1247 1403 CBE
 (56) Documents cited
None
 (58) Field of search
D1P
 (71) Applicant
Colgate-Palmolive Company,
(USA—Delaware),
300 Park Avenue,
New York,
New York 10022,
United States of America
 (72) Inventors
Pallassana N
Ramachandran,
Richard S Parr,
Martin D Reinish
Seymour Grey
 (74) Agent and/or address for service
Kilburn and Strobe,
30 John Street,
London,
WC1N 2DD

(54) **Fabric softening detergent**

(57) A particulate synthetic organic fabric softening detergent composition product of improved appearance and/or flowability is made by mixing together 10 to 60% of detergent composition particles having finely divided bentonite powder adhered to external surfaces thereof and 90 to 40% of similar such detergent composition particles devoid of such bentonite powder on the surfaces thereof. When the detergent composition particles, preferably spray dried, are white and the bentonite is off-colour the described product appears whiter than does a "control" wherein the same total proportion of bentonite is agglomerated onto the surfaces of all the detergent particles. Also, when the

bentonite-surfaced particles are higher in content of tacky detergent than the non-bentonite-surfaced particles, which increased detergent content may be obtained by spraying aqueous detergent solution onto the particles before agglomeration with bentonite powder, the flow properties of the product are improved, compared to a product containing the same total proportion of the detergent evenly distributed throughout all the particles. The bentonite particles are adhered to the detergent composition particles with the aid of an aqueous spray, preferably of a dilute sodium silicate solution, and the agglomerate resulting may be used directly as a detergent composition or may be blended with detergent composition particles not having bentonite on the surfaces thereof.

GB 2 120 695 A

Fig. 1

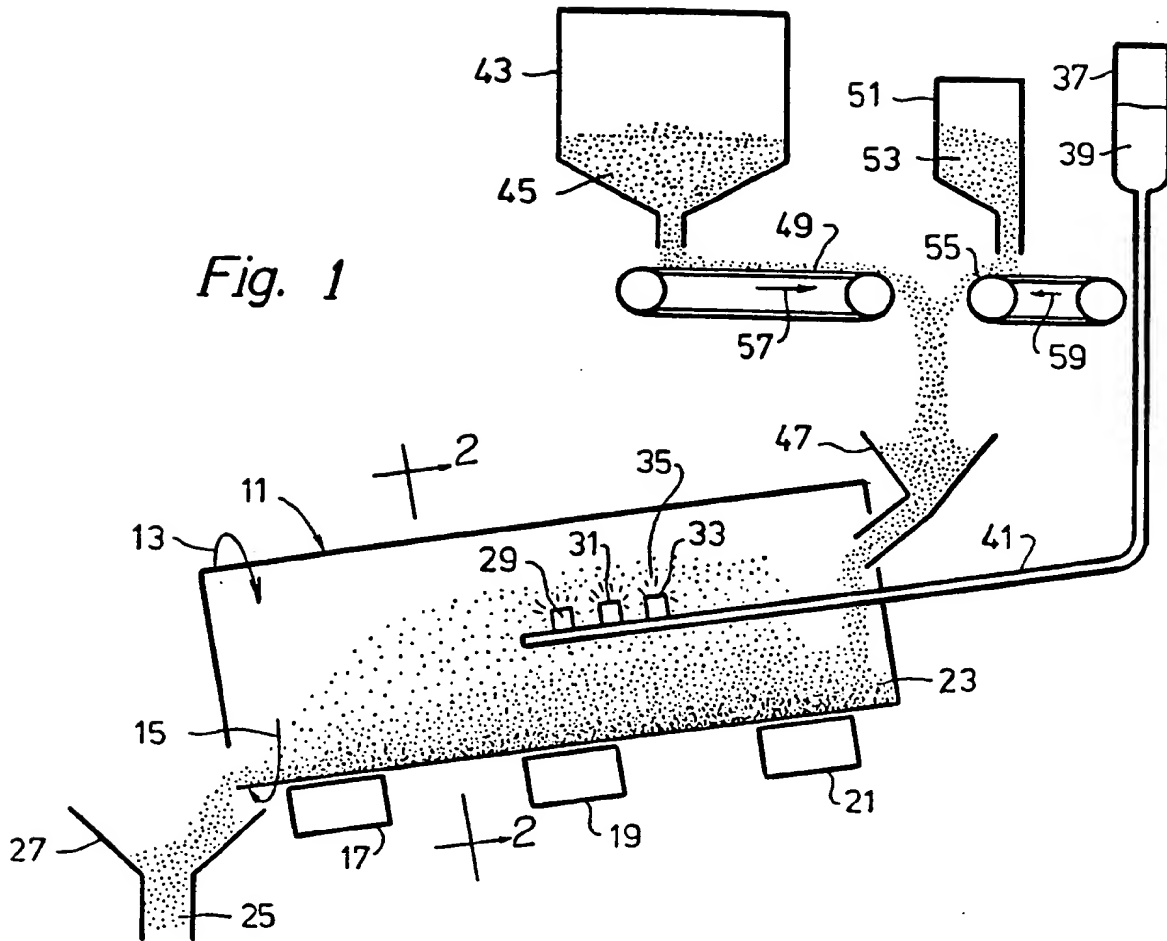
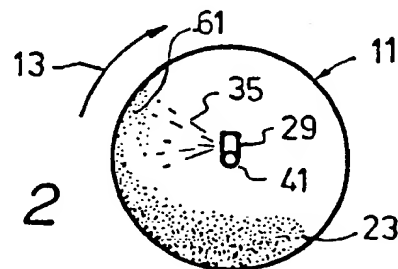


Fig. 2



SPECIFICATION

Fabric softening detergent

This invention relates to particulate synthetic organic detergent compositions and methods for the manufacture thereof. More particularly, it relates to fabric softening detergent compositions containing bentonite, agglomerated from finely divided bentonite powder onto surfaces of larger detergent composition particles, and to processes of effecting such agglomeration.

Spray dried detergent compositions are well known and comprise a major proportion of particulate heavy duty laundry products sold for use in automatic washing machines. Because laundry washed with such compositions may be uncomfortably hard or "boardy", especially if dried on a washing line instead of in an automatic dryer, fabric softeners have been employed, sometimes in the rinse cycle of the washing process and sometimes in an automatic laundry dryer, to deposit softening material onto surfaces of the laundry. Waxy fabric softeners, such as quaternary ammonium halides, have also been included in detergents, but only a minor proportion of such softener will not be discharged with the wash water, leaving little deposited on the laundry. Also, such cationic materials react with anionic detergents and fluorescent brightener dyes and therefore are detrimental. Bentonite has been used in detergent compositions as a filler and as a softening agent. The bentonite particles, of very small ultimate particle sizes, tend to adhere to the material being washed and provide lubricating sites on such material, making it softer to the touch. However, various naturally occurring bentonites, such as Wyoming bentonite, which may be desirably employed as a softening agent in detergent compositions, tend to be off-colour or of a tannish shade, and thereby may adversely affect the appearance of products containing it, which effect is more objectionable when the bentonite is applied as a surface coating to detergent particles or beads (because agglomeration appears to accentuate the bentonite colour and also because the colour is not masked by other constituents of the beads). Also, bentonite, usually being a very finely divided powder, may separate during storage from other detergent composition particles of larger size unless it is attached to them. By means of the present invention such disadvantages of post-added bentonite are overcome. Additionally, the products of the present invention tend to cake less than conventional detergent compositions, are of more uniform appearance than products containing bentonite-only agglomerates mixed with detergent beads, and are of better bead strengths than products wherein the clay is incorporated in the crutcher or post-added as a powder. Also, in one aspect of the invention, flowability of the product is further improved over corresponding products containing tacky materials in the detergent composition formula.

In accordance with a product aspect of the present invention, a particulate synthetic organic detergent product comprises a mixture of 10 to 60% of detergent composition particles having finely divided bentonite powder adhered to external surfaces thereof and 90 to 40% of detergent composition particles devoid of such bentonite powder on the surfaces thereof. In preferred embodiments of this aspect of the invention the detergent composition is in the form of spray dried white beads, the bentonite is an off-white or tannish powder, the bentonite comprises from 20 to 80% of the beads of which it is a surface portion and the bentonite is held to such beads by a small proportion of sodium silicate binder. A further preferred embodiment is one wherein the bentonite-surfaced beads are higher in tacky synthetic organic detergent content than the non-bentonite-surfaced beads.

According to process aspects of the present invention a method of manufacturing a particulate synthetic organic detergent product comprises agglomerating finely divided bentonite powder and larger sized detergent composition particles so that the bentonite powder adheres to the external surfaces of the detergent particles, and blending 10 to 60% of said bentonite-surfaced detergent composition particles with 90 to 40% of non-bentonite-surfaced detergent composition particles. In preferred embodiments of this aspect of the invention the bentonite powder is blended with spray dried built synthetic organic detergent composition beads and is agglomerated onto them by mixing while spraying a dilute aqueous solution of sodium silicate onto the mix.

Such process is also useful for making detergent compositions wherein all the detergent particles have bentonite agglomerated onto them, as when the bentonite is of excellent whiteness, off-colour is not objectionable, or the beads are dyed or pigmented. In accordance with this aspect of the invention a process for manufacturing a fabric softening particulate synthetic organic detergent composition comprises mixing together a minor proportion of a finely divided bentonite powder and a major proportion of larger sized detergent composition particles, spraying onto the surfaces of the mixture, while it is in motion, with new surfaces of the mixing materials being continuously presented to the spray, a minor proportion of an aqueous sodium silicate solution at a concentration in the range of 2 to 8% in such quantity that the spray deposits from about 0.1 to 1.4% of sodium silicate and about 2 to 8% of moisture on the mixture, continuing mixing after application of the aqueous sodium silicate solution, and removing agglomerated particulate detergent with bentonite powder held to the surfaces thereof. Preferably, the bentonite employed is of particle size such that substantially all of it passes through a No. 200 sieve, U.S. Sieve Series (which has openings 74 microns across) (more preferably, all of it passes through a No. 325 sieve, which has openings 44 microns

across), the detergent composition particles are spray dried particles of a built synthetic organic detergent composition of particle sizes in the range of No's. 8 to 100 sieves (U.S. Sieve Series, which have openings 2380 microns and 149 microns across respectively) (more preferably No's. 10 to 60 sieves, U.S. Sieve Series, which have openings 2000 microns and 250 microns across respectively), the sodium silicate is of $\text{Na}_2\text{O}:\text{SiO}_2$ ratio of about 1:2.4, the droplets of the sodium silicate spray are of diameters no greater than one millimeter, (more preferably in the range of 0.1 to 0.5 mm), and the process takes place in a rotary drum type mixer, such as one which extends longitudinally at an angle of from about 2 to 15° to the horizontal, with the initial mixing, the spraying-agglomerating and the subsequent mixing taking place sequentially in an upstream third, a middle third, and a downstream third of the mixer, respectively.

The detergent composition particles which are the base particles used in this invention, some of which are agglomerated with a more finely divided bentonite powder on the surfaces thereof, may be any suitable particles and can be produced in any of various ways. However, it will be much preferred that they be spray dried particles of sizes within the No's. 8 to 100, preferably 8 or 10 to 60 and more preferably 10 to 40 or 60 sieve ranges, U.S. Sieve Series (40 mesh has openings 420 microns across).

Normally such products will comprise a synthetic organic detergent which will be either an anionic or nonionic detergent, a builder for the detergent, adjuvant(s) and moisture. Among the various anionic detergents that may be employed, usually as their sodium salts, those which are most preferred are linear higher alkyl benzene sulphonates, higher alkyl sulphates and higher fatty alcohol polyethoxylate sulphates. Preferably, in the higher alkyl benzene sulphonate the higher alkyl group is linear and averages 11 or 12 to 15 carbon atoms, e.g. 12 to 13, and is a sodium salt. However, other alkyl benzene sulphonates, of 10 or 12 to 18 carbon atoms in the alkyl groups, may also be employed. The alkyl sulphate is preferably a higher fatty alkyl sulphate of 10 to 18 carbon atoms, preferably 12 to 16 carbon atoms, e.g. 12, and is also employed as the sodium salt. The higher alkyl ethoxamer sulphates will similarly be of 10 or 12 to 18 carbon atoms, e.g. 12, in the higher alkyl, which will preferably be a fatty alkyl, and the ethoxy content will normally be from 3 to 30 ethoxy groups per mol preferably 3 or 5 to 20. Again, the sodium salts are preferred. Thus, it will be seen that the alkyls are preferably linear or fatty higher alkyls of 10 to 18 carbon atoms, the cation is preferably sodium, and when a polyethoxy chain is present the sulphate is at the end thereof. Other useful anionic detergents include the higher olefin sulphonates and paraffin sulphonates, e.g. the sodium salts wherein the olefin or paraffin groups are of 10 to 18 carbon atoms. Specific examples of the preferred detergents are sodium tridecyl benzene

sulphonate, sodium dodecyl benzene sulphate, sodium tallow alcohol polyethoxy (3 EtO) sulphate, and sodium hydrogenated tallow alcohol sulphate. In addition to the preferred anionic detergents mentioned, others of this well-known group may also be present, especially in only minor proportions with respect to those previously described. Also mixtures thereof may be employed and in some cases such mixtures can be superior to single detergents. The various anionic detergents are well known in the art and are described at length at pages 25 to 138 of the test *Surface Active Agents and Detergents*, Vol. II, by Schwartz, Perry and Berch, published in 1958 by Interscience Publishers, Inc.

Although various nonionic detergents of satisfactory physical characteristics may be utilized, including condensation products of ethylene oxide and propylene oxide with each other and with hydroxy-containing bases, such as nonyl phenol and Oxo-type alcohols, it is highly preferable that the nonionic detergent, if present be a condensation product of ethylene oxide and higher fatty alcohol. In such products the higher fatty alcohol is of 10 to 20 carbon atoms, preferably 12 to 16 carbon atoms, and the nonionic detergent contains from about 3 to 20 or 30 ethylene oxide groups per mol, preferably from 6 to 12. Most preferably, the nonionic detergent will be one in which the higher fatty alcohol is of about 12 to 13 or 15 carbon atoms and which contains from 6 to 7 or 11 mols of ethylene oxide. Such detergents are made by Shell Chemical Company and are available under the trade names Neodol (Registered Trade Mark) 23—6.5 and 25—7. Among their specially attractive properties, in addition to good detergency with respect to oily marks on goods to be washed, is a comparatively low melting point, which yet is appreciably above room temperature, so that they may be sprayed onto base beads (which may contain builders but usually little or no detergent) as a liquid which solidifies. When nonionic detergents are utilized and are applied to detergent beads as a spray, such spray may be applied exclusively to the beads to be surface coated with bentonite, or part of the nonionic detergent may be spray dried with the builder salt and stable adjuvants. Alternatively, and sometimes preferably (but this is rare) the nonionic detergent may be sprayed onto the agglomerated bentonite-base beads or onto a mixture of such beads with non-bentonite-containing product.

The water soluble builder or mixture of builders employed may be one or more of the conventional materials that have been used as builders or suggested for such purpose. These include inorganic and organic builders, and mixtures thereof. Among the inorganic builders those of preference are the various phosphates, preferably polyphosphates, e.g. tripolyphosphates and pyrophosphates, such as pentasodium tripolyphosphate and tetrasodium pyrophosphate. Tri-sodium nitrilotriacetate (NTA), preferably

employed as the monohydrate, and other nitrilotriacetates, such as disodium nitrilotriacetate, are preferred organic builder salts. Sodium tripolyphosphate, sodium pyrophosphate and NTA may be utilized in hydrated or anhydrous forms. Other water soluble builders that are considered to be effective include the various other inorganic and organic phosphates, borates, e.g. borax, citrates, gluconates, EDTA (ethylene diamine tetraacetic acid) and iminodiacetates. Preferably the various water soluble builders will be in the form of their alkali metal salts, either the sodium or potassium salts, or a mixture thereof, but sodium salts are normally more preferred. The silicates, preferably sodium silicates of $\text{Na}_2\text{O}:\text{SiO}_2$ ratio within the range of 1:1.6 to 1:3.0, preferably 1:2 to 1:2.8, e.g. 1:2.35 or 1:2.4, also serve as water soluble builder salts, but because of their strong binding properties are useful to assist in agglomeration. The content of silicate in the product will normally not exceed 10 or 15%, with the range of 5 to 15% being feasible, preferably 3 to 7 or 8% when zeolite is not present and 0 to 2 or 5% in the presence of zeolite (with only small proportions of silicate being employed as a binder to hold the bentonite to the detergent or detergent base particles when zeolite is present). In some cases it may be desirable to post-add free flowing sodium silicate, such as hydrated sodium silicate particles. In addition to the water soluble builders, water insoluble builders, such as the zeolites, especially zeolite A, preferably hydrated, e.g. containing 20% water, may be substituted, preferably only partially. The bentonite employed is a colloidal clay (aluminium silicate) containing montmorillonite. The type of bentonite clay which is most useful in making the base beads of the present invention is that which is known as sodium bentonite (or Wyoming or western bentonite), which is normally a light to cream-coloured or tannish impalpable powder which, in water, forms a colloidal suspension having strongly thixotropic properties. In water the swelling capacity of such clay will usually be in a range of 3 to 15 or 20 ml/gram, preferably 7 to 15 ml/g, and its viscosity, at a 6% concentration in water, will usually be in the range of 3 to 30 centipoises, preferably 8 to 30 centipoises. Preferred swelling bentonites of this type are sold under the trade name Mineral Colloid, as industrial bentonites, by Benton Clay Company, an affiliate of Georgia Kaolin Co. These materials which are the same as those formerly sold under the trademark Thixojel, are selectively mined and beneficiated bentonite, and those considered to be most useful are available as Mineral Colloid No's. 101, etc., corresponding to Thixo-jels No's. 1, 2, 3 and 4. Such materials have pH's (6% concentration in water) in the range of 8 to 9.4, maximum free moisture contents of about 8% and specific gravities of about 2.6, and for the pulverized grade about 85% passes through a 200 mesh U.S. Sieve Series sieve. Beneficiated Wyoming bentonite is preferred as a component of the

present compositions but other bentonites including the synthetic bentonites (those made from bentonites having exchangeable calcium and/or magnesium by sodium carbonate treatment) are also useful. Also, the particle size may be lowered so that all of the bentonite passes a No. 325 screen (U.S. Sieve Series, which has openings 44 microns across). Although it is desirable to limit maximum free moisture content, as mentioned, it is more important to make certain that the bentonite being employed includes enough free moisture, most of which is considered to be present between adjacent plates of the bentonite, to facilitate quick disintegration of the bentonite and any adjacent materials in the particles when such particles or detergent compositions containing them are brought into contact with water, such as wash water. It has been found that at least about 2%, preferably at least 3% and more preferably, about 4% or more of water should be present in the bentonite initially, before it is admixed with the other bead components in the crutcher, and such proportion should also be present after spray drying or any other drying that is undertaken. In other words, overdrying to the point where the bentonite loses its "internal" moisture can significantly diminish the utility of the present compositions. When the bentonite moisture content is too low the bentonite does not satisfactorily aid in disintegrating the beads in the wash water. When the bentonite is of satisfactory moisture content it may exhibit an exchangeable calcium oxide percentage in the range of about 1 to 1.8 and with respect to magnesium oxide such percentage can be in the range of 0.04 to 0.41. Typical chemical analyses of such materials are from 64.8 to 73.0% of SiO_2 , 14 to 18% of Al_2O_3 , 1.6 to 2.7% of MgO , 1.3 to 3.1% of CaO , 2.3 to 3.4% of Fe_2O_3 , 0.8 to 2.8% of Na_2O and 0.4 to 7.0% of K_2O .

Although some adjuvants, such as fluorescent brightener, pigment, e.g. ultramarine blue, titanium dioxide, polyacrylate, and inorganic filler salt may be added to the crutcher, others, such as perfumes, enzymes, bleaches, some colourants, bactericides, fungicides, and flow promoting agents may often be sprayed onto or otherwise mixed with the base beads or spray dried detergent compositions, with any nonionic detergent to be post-added, and/or independently, so that they will not be adversely affected by the elevated temperatures of the spray drying operation and also so that their presence in the spray dried beads does not inhibit absorption of nonionic detergent, when such is to be post-sprayed onto the beads. However, for stable and normally solid adjuvants, mixing with the starting slurry in the crutcher is also often feasible. Also, any less stable adjuvants may be post-added to the agglomerate.

Of course, water is present in the crutcher to serve as the medium for dispersing the various other bead components, and some water, in both free and hydrate form is in the product. During

drying of the beads the initial moisture content thereof, which will be about 25 to 60%, may be lowered to about 5 to 15%, with such moisture content being sufficient so that the bentonite in the dried beads (normally less than 10% and preferably none is present) contains at least 2% and preferably at least 4% of moisture. It is preferred to employ deionized water, so that the hardness ion contents thereof may be very low and so that metallic ions that can promote decomposition of any organic materials which may be present in the crutcher mix or post-added materials are minimized, but city or tap water may usually be employed instead. Normally the hardness content of such water will be less than about 300 p.p.m., as CaCO_3 , preferably less than 150 p.p.m.

The proportions of the various components in the base beads and in the spray dried detergent composition beads will be such as to result in their being effective cleaning agents, of acceptable flow properties, bulk density and appearance. Preferably, in most cases, they will be white, except that the beads coated with bentonite will often appear darker in colour (off-colour) if examined closely. If desired, a whitening agent may be employed, such as TiO_2 , in an amount from 0.2 to 5% of the bentonite. However, it is within the invention to utilize a colouring dye or pigment in the crutcher mix so that the spray dried beads (or beads otherwise produced) are coloured.

It has been found that satisfactory detergent composition beads can be made comprising 2 or 5 to 30 or 35%, preferably 5 or 15 to 25 or 30%, e.g. 6 or 15% to 20 or 25%, of synthetic organic detergent, preferably anionic detergent, 20 or 30 to 90%, preferably 30 or 35 to 80 or 85%, and more preferably 35 or 45 to 70% of builder, 0.2 or 0.5 to 35 or 40%, preferably 0.5 or 1 to 20 or 30% and more preferably 1 to 10% or 1 to 20% of adjuvant(s), and 3 to 20, preferably 4 to 15% and more preferably 5 to 12% of moisture, e.g. 7 or 8%. Such beads, which may be made by normal spray drying processes, or by other "equivalent" means, will usually be of characteristic globular or other shape known to result from spray drying, often makes ideal nuclei onto which bentonite powder may be agglomerated. They will normally be of bulk densities within the range of 0.2 to 0.7 g/cc, such as 0.3 to 0.5, e.g. 0.35. The particle sizes thereof will normally be in the 8 to 100 range (U.S. Sieve Series) and particles outside such range may be removed by screening or other separating operations. More preferably, the bead sizes will be from No. 8 or 10 to 40 or 60, U.S. Sieve Series, and the beads are white or of some other colour which would appear objectionably affected by application of the commercial tannish or off-colour bentonite particles to the surfaces thereof, even if a colour agent is applied with it in an attempt to duplicate the original bead colour. When the beads containing bentonite on the surfaces thereof are to be used directly, without

blending with detergent beads, it is preferred that they be white, not grey or tan, even if a whitener such as TiO_2 has to be used.

It has been found that when 10 to 60%, by weight, of the detergent composition particles have finely divided bentonite powder agglomerated onto the surfaces thereof, with 90 to 40% of the detergent composition particles being devoid of such powder on the surfaces thereof, the human eye does not note the darkening of the bentonite-surfaced beads and does not detect any objectionable speckling of the product, at least not compared to products of similar composition in which the bentonite powder is evenly distributed over the spray dried beads, or in which bentonite-only agglomerates are used, and so the products of the present invention are not found to be objectionably off-colour by consumers. Preferred ranges are 20 to 50% and 30 to 45%, e.g. 40%, for the bentonite surfaced material, with the balance being uncoated detergent composition particles. The proportion of bentonite, by weight, on the surface of the detergent beads on which it is coated, will normally be with the range of 10 or 20 to 80%, preferably 35 to 65%, more preferably 40 to 60%, e.g. 50% for the product to be blended with bentonite-free detergent particles. For the agglomerated particles to be used directly (no blending with detergent particles) such ranges are 10 to 30%, preferably 15 to 25%, e.g. 20% of the product. It is found that because the spray dried beads are not solid, the applications of these comparatively large quantities of bentonite do not change the particle sizes dramatically, although there may be some increase, such as about 5 to 15 or 30%, in bead diameters. The relatively slight increase in the bead dimensions does not create settling or "floating" problems and the presence of the bentonite on the bead exterior appears to help inhibit separations of different sized particles on storage (compared to smooth, surfaced, similarly non-tacky beads). Also, it does not cause objectionable changes in product bulk density.

The application of bentonite to the detergent composition beads (which in some cases may be inorganic builder beads, as when nonionic detergent is to be post-added) may be effected by standard agglomeration techniques and equipment, such as a rotary drum type mixer-agglomerator like that shown in the drawings described below. One process that has been found to be especially useful is to mix the desired weights of the detergent composition beads and finely divided bentonite powder and while mixing, spray water or more preferably, spray a dilute sodium silicate solution onto the moving surfaces thereof. Such sprayings may be at room temperature and will be gradual enough so as to prevent any objectionable lumping of the mixture. Mixing will continue in known manner until the bentonite powder is all held to the detergent beads, after which mixing may be halted and the product may be screened or otherwise size-classified to be within the desired product size

range. The silicate solution employed when the agglomerate is to be mixed with detergent particles will normally be at a concentration of 0.05 to 10%, such as 0.2 to 6%, e.g. 1, 2 or 4%.

- 5 Enough will be employed so that on the beads on which it is present it will constitute from 0.01 to 2%, such as 0.02 to 0.2 or 0.4%. At such application concentrations satisfactory agglomeration and surface coating are obtained,
- 10 using suitable agglomerating equipment, such as an O'Brien agglomerator, or a conventional inclined drum equipped with spray nozzles, baffles, etc. Also, the moisture sprayed onto the beads is not excessive, usually being about 1 to
- 15 10% of the bead weight, e.g. 2 to 5%, which will be less on the basis of the final product. The product resulting is sufficiently firm to be able to withstand handling, packaging and storage without objectionable powdering and loss of the bentonite coating. Also, the silicate concentration is not so high as to inhibit dispersion of the bentonite in the wash water when the product is employed in laundry operations. Although it is preferred that silicate be employed in the
- 25 agglomerating spray, useful product is obtainable by utilizing water alone as an agglomerating agent or by employing aqueous solutions of other binders, such as gums, resins, surface active agents (detergents), but in the absence of such
- 30 material the bentonite, which has binding properties, will normally be cohesive enough to make coated particles of desired physical stability, which will rapidly disperse in the wash water. If desired, a dye may be applied in the liquid spray
- 35 utilized in agglomeration, so as to colour the resulting particles. Normally the dye concentration will be less than 1% of the liquid being sprayed, e.g. 0.01 to 0.1% thereof. By employing the dye for only the bentonite surfaced particles the resulting detergent product will have an attractive appearance and the "softener
- 40 particles" will be dye-identified. If it is desired to have the product all coloured (and blue is a preferred colour), the base beads may also be coloured. Specifically, ultramarine blue pigment may be crutched in with the other components of the spray dried detergent composition and Acilan blue or Polar Brilliant blue (dyes) may be sprayed
- 45 onto the surfaces of the agglomerated bentonite particles.

- 50 In a variation of the present invention, the flowability of the resulting product can be improved by incorporating some or all of the most tacky components of the final product in the beads to
- 55 be bentonite-surfaced. Then, such beads are coated with a protective film of agglomerated finely divided bentonite particles and the tacky component is buried below the bentonite surface, thus being ineffective to inhibit free flow. The
- 60 other particles of the detergent, not containing such component, flow more freely than would be the case if it was included in their composition, too. Additionally, the tacky material may act to promote agglomeration of the bentonite and the
- 65 firm holding thereof to the surfaces of the base

particles. In fact, in another version of the invention some or all of the synthetic organic detergent, either an aqueous solution of anionic detergent or a liquid state nonionic detergent, is sprayed onto the detergent composition base particles before mixing thereof with the bentonite. This post-spraying of the detergent, rather than incorporating it (or some of it) in the crutcher and spray drying it, improves the spray drying operation and increases spray tower throughput rates. Of course, in situations where flowability is not a problem and where relatively large proportions of nonionic detergent are to be post-sprayed onto the detergent composition based bead surfaces, it may not be necessary or desirable to apply all the detergent or more than a pro rata share of it to the bentonite-surfaced beads but where flowability is unsatisfactory this aspect of the present invention provides means for improving it significantly. When at least a part of the synthetic organic detergent is to be spray dried in the base beads then normally the beads to be coated with bentonite will have at least 10%, preferably 25% and more preferably 50%

70 more of detergent than the rest of the beads.

- After the bentonite-surfaced beads are produced they may subsequently be mixed with materials to be post-added or such materials may be sprayed onto the bead surfaces but normally
- 95 the bentonite-surfaced beads will first be mixed with the balance of the spray dried detergent composition material, after which any post-added material may be applied or mixed with them. Among such materials are enzyme powders, bleaches and perfumes. Alternatively, some of
- 100 said materials may be applied to or with some of them before the bentonite-surfaced beads and other beads are mixed together. It is also possible to post-add some of the adjuvants to the detergent beads before application of the bentonite to such beads but such method is not usually practiced. After mixing together of the different portions of the present compositions, they may be stored for a curing period of one to
- 105 twenty-four hours, for example, but usually there will not be any need for such a cure, and they may then be mixed with any adjuvants, unless such was accomplished earlier. They may then be transported to packaging equipment, and may be
- 110 packed, cased, stored and/or shipped.

- The products resulting from this invention, as previously described, when detergent composition beads are white, will appear noticeably whiter than corresponding products in
- 120 which the bentonite to be applied is distributed evenly over all the particles. This phenomenon appears to depend on the proportions of the beads, and to some extent, on the particle sizes thereof. Also of importance is that the products of the present invention do not appear speckled though they do contain white and tannish particles. Yet, they appear uniform and are light of colour. When lesser proportions of bentonite-surfaced particles than the lower limit of the
- 125

broadest range specified herein are employed, while the darker colour of such particles may not be objectionably noticeable, the bentonite content of the product will usually be less than desirable.

- 5 When a greater proportion of bentonite-surfaced particles than the upper limit of the broadest range given are employed the product will be noticeably darker and off-colour and its appearance will be objectionable to the average consumer, making it difficult to market. Specific reflectance differences are not given herein because of the varying natures of the natural and synthetic bentonites available commercially and their different shades, but differences are
- 15 noticeable by use a reflectometer, such as a Hunter reflectometer, or by use of a spectrophotometer, such as one made by General Electric Company. However, it is usually not necessary to employ instrumentation to detect the differences
- 20 in colour because these are so readily apparent to the eye of the average consumer. When different percentages of detergent are present in the bentonite-surfaced and non-bentonite-surfaced beads, as previously taught, and when detergent
- 25 is applied to the beads to be coated with bentonite, improvements in product flowability are noted and the products resulting are noticeably less tacky to the touch and tend less to clump in the box on storage. Such improvements
- 30 in these properties are verifiable by standard tests employed in the detergent industry, such as flow-time, angle-of-repose and compaction tests.

As will be evident, the properties of the final detergent product are improved without need for

35 adjuvants to improve colour, flow or non-tackiness. Thus, the expenses of such adjuvants and their sometimes undesirable other properties are avoided. Because only a portion of the detergent beads is subjected to agglomeration,

40 throughput times for the agglomerating equipment are diminished. Thus, both composition and process advantages are obtained and the final product is surprisingly improved, compared to one containing the same total

45 proportion of bentonite coating all the detergent composition particles.

The invention may be put into practice in various ways and a number of specific embodiments will be described to illustrate the

50 invention with reference to the accompanying examples and drawings in which:

Figure 1 is a schematic central longitudinal sectional elevational view of a rotary drum type mixer, with other equipment which may be

55 utilized in the practice of process aspects of the present invention; and

Figure 2 is a transverse sectional view of the said rotary drum along the line 2—2, showing the spraying of silicate solution onto tumbling

60 particles of detergent composition and bentonite.

Unless otherwise indicated throughout this specification all parts are by weight and all temperatures are in °C.

Example 1

		Percent
65	Sodium linear tridecylbenzene sulphonate	12
	Pentasodium tripolyphosphate, hydrated	34
70	Sodium silicate ($\text{Na}_2\text{O}:\text{SiO}_2=1:2.4$)	7
	Sodium sulphate	12
	Borax	2
	Sodium carboxymethyl cellulose	0.5
75	Bentonite (Mineral Colloid 101, 200 mesh (U.S. Sieve Series openings 74 microns across), 7% H_2O)	20
80	Perfume	0.5
	Moisture	12.0
		<hr/> 100.00

- A detergent composition of the above formula is made by spray drying a mixture of the
- 85 components of such composition, except for the bentonite and perfume (and with slightly less silicate, to allow for that post-added), at a crutcher mix moisture content of about 35% in a standard commercial countercurrent spray drying
- 90 tower under normal conditions, with the drying air temperature in the range of 200 to 400°C, to produce globular beads of normal particle size distribution in the range of No's. 10 to 100, U.S. Sieve Series (10 mesh has openings 2000
- 95 microns across, 100 mesh 149 microns across). One part of such beads is transferred to an O'Brien agglomerator or similar agglomerating apparatus and is mixed therein with an equal weight of the bentonite, and while mixing is
- 100 continued there is sprayed onto the moving surfaces of the particles an aqueous solution (at room temperature) containing 5% of sodium silicate, with the total proportion of spray applied being about 0.04 part. Agglomerating is
- 105 continued for about 20 minutes, during which time some moisture evaporates and after which substantially all the particles are in the 8 to 100 sieve size range (U.S. Sieve Series, 8 mesh has openings 2380 microns across). Particles outside
- 110 this range are removed and 1.5 times the weight of the remaining particles (omitting added water) of the spray dried detergent beads, devoid of bentonite coating, are then blended with the bentonite-surfaced beads in a tumbling drum for a
- 115 period of twenty minutes, after which the product is perfumed and packed in cartons. The spray dried detergent employed herein has a moisture content of about 8 to 10% but this can be changed by using beads and bentonite of other
- 120 moisture contents and varying the spray accordingly. The product made, when it is compared with a control product, made in similar manner but with the bentonite being coated onto all the detergent particles (with the total
- 125 proportion of bentonite being the same as in the final product of the invention), appears lighter in

colour, uniform in appearance (not "spotty"), and more attractive to the human eye, making it more acceptable to the consumer. To make a coloured product 0.2% of ultramarine blue pigment may be in the spray dried beads, with 0.004% of Acilan blue being on the bentonite agglomerates to match colour. When silicate is omitted from the agglomerating spray a satisfactory product can also be made but upon aging such a product may be significantly more friable.

When the above described procedures are varied by blending 0.3 part of enzyme powder (Alcalase, 2 Anton units per gram) in prilled or powder form (prills within the 10 to 100 mesh range and powder through 200 mesh) before perfuming, the improvement in the appearance of the product is still evident.

The various products of this example are all satisfactory fabric softening particulate detergents, useful in automatic washing machines for heavy duty washing of soiled laundry.

Example 2

A product of the formula of that of Example 1 is made by spray drying two different compositions, one containing 24% of sodium linear tridecylbenzene sulphonate and the other containing 12% thereof. The difference is made up by decreasing or increasing the sodium sulphate contents of the respective formulas. The product higher in anionic detergent content (and lower in sulphate) is tackier to the touch and it is this product which is coated with an equal weight of bentonite powder (through a No. 325 sieve (U.S. Sieve Series which has openings 44 microns across)) and which is subsequently blended with 1.5 times the weight of the resulting agglomerate (which is agglomerated in the same way as in Example 1) of the non-bentonite-surfaced beads, which are lower in anionic detergent content. The mixture is then perfumed in the normal manner.

The product resulting is of improved flowability compared to the product of Example 1, apparently due to the "insulating" effect of the bentonite particles agglomerated onto the surfaces of the beads higher in anionic detergent content. Also, due to the tackiness of such beads, the amount of silicate solution applied may be reduced, sometimes to half that employed in Example 1. In addition to making a product which is more free flowing, less tacky and less susceptible to caking on storage than the products of Example 1 (which products are acceptable for commercial purposes), the presence of the greater proportion of anionic detergent in the bentonite-containing beads promotes more rapid disintegration and dispersion of such beads in the wash water, which improvement is aided by the presence of a lesser proportion of silicate in the surfacing bentonite material. In some instances, as in Example 1, the silicate may be omitted from the agglomerating spray or equal proportions of other binding materials, such as sodium polyacrylate,

polyvinyl pyrrolidone or hydroxypropylmethyl cellulose may be substituted. An additional advantage of the process of this example is that bentonite fines, sometimes present with the bentonite agglomerate, are reduced, this being attributable to the tacky detergent, in part.

Example 3

The procedure of Example 1 is varied by decreasing the anionic detergent content of the spray dried beads from 15% to 14% and spraying the remaining anionic detergent onto the surface of the portion of the beads to be coated with bentonite particles, and in the agglomerating spray. The sprayed material is of a solids concentration of about 10% in water and if the product made becomes too sticky, heat and air flow may be employed to lower the moisture content to reduce such stickiness to an acceptable "tacky" level. The detergent composition resulting, after mixing of the bentonite-surfaced beads with the non-bentonite-surfaced beads, is of properties comparable to that of Example 2.

Example 4

When the sodium linear tridecylbenzene sulphonate of Example 1 is replaced by sodium hydrogenated tallow alcohol polyethoxy (3 EtO) sulphate, sodium hydrogenated tallow alcohol sulphate, sodium paraffin sulphate or sodium olefin sulphonate of 16 carbon atoms in the paraffin and olefin groups, or by any two-component mixtures thereof (of equal parts) products comparable in properties to those of Example 1 are obtained. This is also the case when the total of the pentasodium tripolyphosphate and sodium sulphate contents is replaced by pentasodium tripolyphosphate, sodium carbonate, sodium bicarbonate, zerolite A or equal part two component mixtures thereof. Also, when the proportion of bentonite applied to the bentonite-surfaced beads is varied to 15 and 25% acceptable products of improved appearance are obtained, which is also the case when the proportion of bentonite-surfaced particles is changed to 15 and 25%, respectively.

Example 5

	Percentages
Sodium carbonate	22
Sodium bicarbonate	16
Zeolite A, hydrated (20% moisture)	32
Fluorescent Brightener (Tinopal)	1.5
Moisture	9.0
Perfume	0.5
Nonionic detergent (Neodol 23—6.5)	19
	<hr/> 100.00

Detergent beads of the above composition are

made by spray drying from a 60% solids crutcher mixture beads of the indicated particle sizes comprising all the described constituents except the perfume and nonionic detergent, which are post-sprayed onto such moving bead surfaces (although preferably perfume is applied to the bentonite-containing beads after agglomeration). Due to the content of zeolite A the nonionic detergent is satisfactorily absorbed. Then, one part of such composition is surface-agglomerated with one part of bentonite powder (—325 mesh less than 325 mesh (U.S. Sieve Series) i.e. all passed a meshing having openings 44 microns across) which appears tannish after coating such particles. After the agglomeration is completed 1.5 parts of non-bentonite-containing detergent composition beads are blended with the bentonite-surfaced product. The final product is an excellent softening detergent of the heavy duty nonionic built detergent type and is of whiter appearance than a control wherein the bentonite is surface agglomerated onto all the particles (at the same total concentration of bentonite). The product is a satisfactory heavy duty laundry detergent.

In a modification of this invention a small proportion, 0.1%, of blue dye (Acilan blue), in the silicate solution, is sprayed onto the surfaces of the particles in the agglomerator to colour such particles.

When variations are made in the manufacturing method whereby more nonionic detergent, e.g. 1/10 to 1/4 more, is sprayed onto the beads to be coated with bentonite than onto the beads not to be so coated, flowability is improved and the product made is less tacky.

The foregoing description relates primarily to the aspects of this invention which involve making a fabric softening detergent product of improved colour (or appearance) and flowability.

The making of a detergent composition in which bentonite is agglomerated onto detergent particles will now be described in more detail with reference to the accompanying drawings. It will be understood that the resulting composition may be blended with detergent composition particles or may be used without such blending.

Figure 1 shows an open ended, inclined, cylindrical rotary drum 11 rotating about an axis which is at a relatively small acute angle to the horizontal (e.g. about 10°), with such rotation being in the direction shown by the arrows 13 and 15. The drum 11 rests on rollers 17, 19 and 21, which rotate in the opposite direction from the drum (counterclockwise, rather than clockwise, viewed from the left), causing it to turn as indicated. The rotary drum 11 contains a mixture 23 of spray dried built synthetic organic detergent beads and bentonite powder which is agglomerated in the drum into fabric softening detergent compositions beads or particles, due to the spraying of a dilute sodium silicate solution onto the particles while the mixture is in motion. Final agglomerated softening detergent particles

25 are removed from the drum 11 via a chute 27.

Spray nozzles 29, 31 and 33 are employed to produce essentially conical sprays of silicate solution, such as those represented by numeral 35, which impinge on the moving mixture of detergent beads and bentonite powder and promote agglomeration of the powder onto the surfaces of the beads although in some instances agglomerates may also be formed of bentonite alone or detergent beads alone (the latter being less common). In the rotating drum, the right or upstream third or similar part is a mixing zone wherein the bentonite and detergent beads are dry mixed, the middle portion is a spraying and agglomerating zone, and the downstream third or so is one wherein spraying is not effected, the moistened particles and agglomerates are "finished" to relatively free flowing product, and the desired form and character of the agglomerate results.

The foregoing description relates primarily to a rotary drum which is a preferred embodiment of the apparatus employed in the practice of this aspect of the invention although other equivalent or substitute means may also be utilized. In addition to the rotary drum, supply means for adding the various final product constituents are provided. Thus, a supply tank 37 contains sodium silicate solution 39 (as distinguished from spray 35), which is delivered to the spray nozzles 29, 31 and 33 through a line 41. A hopper bin 43 contains detergent beads 45 which are delivered to a hopper 47 by means of a delivery belt 49. Similarly, a hopper bin 51 contains bentonite powder 53 which is delivered to the hopper 47 by a delivery belt 55. The arrows 57 and 59 indicate the directions of such belt movements, respectively.

In Figure 2 the mixture 23 in the drum 11 is shown being carried up the wall on the left-hand side of the drum, which is rotating in the direction of the arrow 13. As the mix 23 falls downwardly along the face 61 of the upper part of the wall thereof the spray 35 of aqueous silicate solution, sprayed in conical patterns from the nozzle 29 (and other hidden nozzles 31 and 33 masked thereby in this view), impinges on the moving mixture, moistens the surfaces of the nucleus detergent composition beads and promotes agglomeration of the bentonite with the beads, with the more finely divided bentonite powder usually adhering to the surfaces of the larger detergent composition particles. Thus, constantly renewing faces or curtains of falling particles are contacted by the sprays and substantially uniform moistening and application of the silicate to the particles is obtained, which leads to production of a more uniform and better agglomerated product.

The detergent composition particles, bentonite, silicate, adjuvants, etc. employed in the agglomeration process just described are those previously recited in this specification.

When the agglomerated detergent particles, with bentonite on the surfaces thereof, are to be used directly a silicate solution will preferably be used to bind the bentonite to the detergent

particles. While the solution concentrations and proportions previously mentioned may be used usually the silicate solution concentration will be 2 to 8%, preferably 3 to 7% and more preferably 3 to 6%, e.g. 4% and 5%. Enough will be employed so that on the beads on which it is present the silicate from the spray will constitute from 0.1 to 0.4%, preferably 0.2 to 0.3% of the final product weight. At such application concentrations and amounts satisfactory agglomeration and surface coating are obtained, using the rotary drum or other suitable agglomerating equipment. Also the moisture sprayed onto the beads is not excessive, usually being about 3 to 6% of the product weight. Allowance can be made for this added moisture by making the detergent composition beads drier by a corresponding amount.

As with the previously described products, that which results is sufficiently firm to be able to withstand handling, packaging and storage without objectionable powdering and loss of the bentonite coating. Also, the silicate concentration is not so high as to inhibit dispersion of the bentonite in the wash water when the product is employed in laundry operations. If desired, a dye may be applied in the liquid spray utilized for agglomeration, so as to colour the resulting particles. Normally the dye concentration will be less than 1% of the liquid being sprayed, e.g. 0.01 to 0.1% thereof.

After the bentonite-surfaced beads are produced they may subsequently be mixed with materials to be post-added or such materials may be sprayed onto the bead surfaces. Among such materials are enzyme powders, bleaches and perfumes. Alternatively, some of the said materials may be applied to or mixed with the base beads or the bentonite before agglomeration. After agglomeration is completed the products may be stored for curing period of one to twenty-four hours, for example, but usually there will not be any need for such a cure, and the agglomerates may be mixed directly with any adjuvants, unless such was accomplished earlier. The agglomerated beads so made are good detergents possessing significant softening properties. They are also free flowing, non-dusting and substantially non-friable, and possess good bead strengths and abrasion resistance.

The following examples additionally illustrate the invention.

Example 6

A crutcher slurry is made comprising 1,009 parts of water, 2,584 parts of a detergent base (about 37% active ingredient and about 20% of sodium sulphate, with the balance being water), 841 parts of sodium silicate ($\text{Na}_2\text{O}:\text{SiO}_2=1:2.4$), 1,315 parts of pentasodium tripolyphosphate, 542 parts of soda ash, 24 parts of sodium sulphate and 293 parts of an aqueous solution of fluorescent brightener, anti-redeposition agent, stabilizer, and other minor components in dilute aqueous solution. Crutching is in a commercial plant detergent crutcher at a temperature of

about 55°C for a period of about ten minutes after addition of all the components, with the solids content of the crutcher mix being adjusted to about 58°C during the crutching. The crutcher mix is subsequently pumped to a countercurrent spray drying tower wherein it is forced through eight nozzles of the 10/10 type at a temperature of 52°C under a pressure of about 24 kg/sq cm. The lower temperatures are: $T_1=410^\circ\text{C}$ and $T_2=120^\circ\text{C}$. The detergent beads produced are at a moisture content of about 7% and the spray rate is about 9,000 kg/hr. The beads made are screened to be in a size range of 10 to 60, U.S. Sieve Series (which have openings 2000 microns and 250 microns across respectively). The beads are white and are of a bulk density of about 0.3 g/ml.

Equipment essentially like that illustrated in Figures 1 and 2 is employed to agglomerate finely divided bentonite onto the surfaces of the described spray dried detergent composition beads. To make the desired approximately 20% bentonite products No. 325 sieve bentonite powder (containing about 5% of moisture) is mixed with the detergent composition beads in a proportion of 76.4 parts of the base beads to 19.2 parts of the bentonite. 3.8 Parts of a 5% sodium silicate solution ($\text{Na}_2\text{O}:\text{SiO}_2=1:2.4$) are sprayed onto the tumbling mixture in the rotary drum agglomerator-mixer, utilizing a spray lance having six nozzles (three are illustrated in the drawing) spaced apart about 0.5 metre. The spray pressure is about 5 kg/sq cm, which produces a misty spray in which the individual droplets are of diameters within the range of about 0.1 to 0.5 mm (weight average). After about eight minutes total mixing in the rotary drum, which is at an angle of about 7°, with about the last third of the drum being free of silicate spray application, the product is continuously removed, after which it is perfumed with 0.2 part of a suitable perfume and has 0.4 part of enzyme powder blended with it. In a variation of the process the enzyme may be blended with the product in the tumbling drum, in the last third thereof, with or without perfume.

The product resulting is an especially useful fabric softening particulate detergent, which may be screened, if desirable, so as to be in the No's. 10 to 60 range (U.S. Sieve sizes having openings 2000 microns and 250 microns across respectively) or the 8 to 100 sieve range (U.S. Sieve sizes having openings 2380 microns and 149 microns across respectively), as desired. The bulk density of the product is about 0.35 or 0.4 g/ml and it comprises about 18% of sodium dodecyl benzene sulphonate, 25% of sodium polyphosphate, 9.5% of sodium silicate, 9% of soda ash, 10% of sodium silicate, 19% of bentonite, 0.4% of enzyme powder, 0.2% of perfume, 0.1% of fluorescent brightener and 9% of water. The detergent beads are free flowing, non-tacky, sufficiently strong for commercial marketing, readily dispersable in wash water and attractive in appearance. In short, the product is

an excellent fabric softening heavy duty particulate laundry detergent.

Example 7

The procedure of Example 6 is followed except
5 that the silicate solution applied is 3% of sodium silicate and the proportion of solution applied is 4% of the total final product. Flowability, bead strength, non-friability and abrasion resistance are satisfactory, like that of the product of Example 6,
10 and the product is a satisfactory heavy duty fabric softening detergent composition. Similarly, when the same proportion of 6% sodium silicate solution is utilized good results are also obtained. However, when the silicate solution is at 10%
15 concentration the product is less satisfactory, being lumpy in appearance. When only water is employed as the spray an agglomerate is obtainable but it tends to be higher in fines and generally less satisfactory than those
20 agglomerates which are made using the sodium silicate solution at 2 to 8% concentration. From these experiments and others in which the proportion of silicate solution spray is varied it is concluded that better products are obtained when
25 the proportion of spray is about 2 to 8% (moisture basis) of the product and the silicate deposited in the spray is from 0.1 to 0.4% of such product.

Example 8

The procedure of Example 6 is varied by
30 omitting the soda ash from the crutcher mix and replacing it with sodium sulphate. Also, modifications may be made in the location of the spray nozzles in the agglomerating rotary drum, so that the bentonite and detergent composition
35 beads are mixed in the first quarter of the drum, spraying takes place in the middle half, and subsequent mixing takes place in the end quarter. The product resulting is also a satisfactory fabric softening particulate heavy duty detergent like
40 those of Examples 6 and 7. When a blue dye, such as Polar Brilliant blue, is present at a concentration of 0.2% in the silicate spray solution (or from 0.01 to 0.4%) attractively coloured product results. Ultramarine blue and
45 other pigments may be substituted for the dye or may be used with it.

Example 9

Changes in the crutcher mix formulations, temperatures, mixing times and mixing
50 procedures are made and different spray drying tower conditions are employed to produce the detergent composition base beads. Variations of $\pm 10\%$ and $\pm 20\%$ are made in the different formula ingredients of Examples 6—8 and in the
55 mixing times, nozzle pressures and other conditions (but such variations are kept within the described ranges) and a good base bead is made, having a bulk density in the range of 0.3 to 0.5. Also, changes are made in the nozzle designs,
60 pressures and silicate concentrations for the spray solutions, as previously described, and so long as the silicate concentration, amount of solution

applied and silicate deposited with the bentonite on the base beads are within the ranges
65 previously given good products result. Such is also the case when the concentration of bentonite in the final product agglomerate is varied within the range of 15 to 25%. Also, similar results are obtainable when the detergent beads
70 agglomerated with bentonite are nonionic detergents made by spraying nonionic detergent in liquid state onto base inorganic builder beads, after which agglomeration with bentonite and aqueous sodium silicate solution is effected.

75 Good products are also obtained when instead of employing the very finely divided bentonite (through No. 325 sieve), such as the Thixo-Jel No. 1 (Mineral Colloid No. 1,001) used for these examples, other bentonites are used, such as
80 those produced by American Colloid Company and those made from European and other bentonites having exchangeable calcium and/or magnesium ions therein converted to sodium ions by sodium carbonate treatment.

85 Claims

1. A particulate synthetic organic detergent product comprising a mixture of 10 to 60% of detergent composition particles having finely divided bentonite powder adhered to external
90 surfaces thereof and 90 to 40% of detergent composition particles devoid of such bentonite powder on the surfaces thereof.

2. A product as claimed in Claim 1 in which the particles are of sizes within the range of No's. 8 to
95 100 sieves (U.S. Sieve Series, 8 mesh having openings 2380 microns and 100 mesh 149 microns across) and the sizes of the bentonite-surfaced particles are substantially the same as or larger than those of the other detergent particles.

3. A product as claimed in Claim 1 or Claim 2 in which the detergent composition particles are spray dried beads, the agglomerate particle sizes are in the range of No's. 8 to 60 sieves (60 mesh has openings 250 microns across) and the
100 individual bentonite particles that are adhered to the detergent composition particles are of sizes such that they pass a No. 200 sieve (which has openings 74 microns across).

4. A product as claimed in any one of Claims 1
110 to 3 in which the bentonite is held to the detergent bead on which it is coated by sodium silicate, which holding silicate is from 0.01 to 2% of the bentonite agglomerate particles.

5. A product as claimed in any one of Claims 1
115 to 4 in which the bentonite-surfaced particles are higher in content of tacky detergent composition component(s) than the non-bentonite-surfaced particles.

6. A product as claimed in any one of Claims 1
120 to 5 in which the spray dried beads are white, the bentonite covered beads are off-colour, due to the natural colour of the bentonite, and the proportions of bentonite-surfaced and non-bentonite-surfaced beads are such that the product appears uniformly light coloured and
125

particle colour differences are not readily apparent to the human eye.

7. A product as claimed in any one of Claims 1 to 5 in which the detergent particles are white spray dried beads, the bentonite surfaced beads are off-colour, due to the natural colour of the bentonite, and the proportions of bentonite-surfaced and non-bentonite-surfaced beads are such that the product is light coloured and the off-colour bentonite-surfaced beads are not readily apparent to the human eye.

8. A product as claimed in Claim 1 substantially as specifically described herein with reference to the accompanying examples.

9. A process for manufacturing a particulate synthetic organic detergent product which comprises agglomerating finely divided bentonite powder and larger sized detergent composition particles so that the bentonite powder adheres to the external surfaces of the detergent particles, and blending 10 to 60% of said bentonite-surfaced detergent composition particles with 90 to 40% of non-bentonite-surfaced detergent composition particles.

10. A process as claimed in Claim 9 in which the detergent composition particles are spray dried beads of sizes within the range of No's. 8 to 100 sieves, and the bentonite powder agglomerated onto the detergent composition beads surfaces is of particle sizes, before agglomeration, such that substantially all thereof passes through a No. 200 sieve.

11. A process as claimed in Claim 9 or Claim 10 in which the agglomeration is effected by mixing the bentonite powder and the spray dried detergent composition particles while spraying water or a dilute aqueous solution of sodium silicate onto the surfaces thereof.

12. A process as claimed in Claim 9, 10 or 11 in which the spray dried beads are white and the bentonite is off-white.

13. A process as claimed in any one of Claims 9 to 12 in which the proportion of bentonite mixed with and agglomerated onto the surfaces of the beads on which it is to be present is from 20 to 80% thereof.

14. A process as claimed in any one of Claims 9 to 14 in which the agglomeration is effected by mixing the bentonite powder and the spray dried detergent composition particles while spraying onto the surface thereof a dilute aqueous solution of sodium silicate, and the sodium silicate is of $\text{Na}_2\text{O}:\text{SiO}_2$ ratio in the range of 1:1.6 to 1:3.2, the concentration thereof in the aqueous spray is from 0.05 to 10% and the proportion thereof in the final product, acting as a binder to hold the bentonite powder to the spray dried beads on which it is present, is from 0.01 to 2%.

15. A process as claimed in any one of Claims 9 to 14 in which tacky detergent is sprayed onto the surfaces of the detergent composition particles prior to agglomeration of the finely divided bentonite powder therewith.

16. A process as claimed in Claim 9 substantially as specifically described herein with

reference to the examples.

17. A process for manufacturing a fabric softening particulate synthetic organic detergent composition which comprises mixing together a minor proportion of a finely divided bentonite powder and a major proportion of larger sized detergent composition particles, spraying onto the surfaces of the mixture, while it is in motion, with new surfaces of the mixing materials being continuously presented to the spray, a minor proportion of an aqueous sodium silicate solution at a concentration in the range of 2 to 8% in such quantity that the spray deposits from about 0.1 to 0.4% of sodium silicate and about 2 to 8% of moisture on the mixture, continuing mixing after application of the aqueous sodium silicate solution, and removing agglomerated particulate detergent with bentonite powder held to the surfaces thereof.

18. A process as claimed in Claim 17 in which the bentonite powder is of particle sizes, before agglomeration, such that substantially all of it passes through a No. 200 sieve, the detergent composition particles are of sizes, before agglomeration, within the range of No's. 8 to 100 sieves.

19. A process as claimed in Claim 17 or Claim 18 in which the bentonite is from about 10 to 30% of the fabric softening detergent composition produced.

20. A process as claimed in Claim 17, 18 or 19 in which the sodium silicate is of $\text{Na}_2\text{O}:\text{SiO}_2$ ratio in the range of 1:1.6 to 1:3.2.

21. A process as claimed in Claim 20 in which the sodium silicate is of $\text{Na}_2\text{O}:\text{SiO}_2$ ratio within the range of 1:2 to 1:3.

22. A process as claimed in any one of Claims 17 to 21 in which the concentration of the sodium silicate in the aqueous spray is within the range of 3 to 7%.

23. A process as claimed in Claim 17 in which the bentonite powder is of particle sizes, before agglomeration, such that substantially all of it passes through a No. 200 sieve, the detergent composition particles are of sizes, before agglomeration, within the range of No's. 8 to 100 sieves, the bentonite is from about 10 to 30% of the fabric softening detergent composition produced, the sodium silicate is of $\text{Na}_2\text{O}:\text{SiO}_2$ ratio in the range of 1:1.6 to 1:3.2 and the concentration of the sodium silicate in the aqueous spray is within the range of 3 to 7%.

24. A process as claimed in any one of Claims 17 to 23 in which the bentonite is a swelling bentonite.

25. A process as claimed in any one of Claims 17 to 24 in which the detergent composition is a spray dried built synthetic organic detergent composition.

26. A process as claimed in any one of Claims 17 to 25 in which the aqueous sodium silicate spray droplets are of weight average diameter no greater than one millimeter.

27. A process as claimed in any one of Claims 17 to 26 in which the mixing, spraying,

agglomerating and subsequent mixing take place continuously in a rotary drum type mixer.

28. A process as claimed in Claim 17 or Claim 23 in which the bentonite is a swelling bentonite, the detergent composition is a spray dried built synthetic organic detergent composition, the sodium silicate is of $\text{Na}_2\text{O}:\text{SiO}_2$ ratio within the range of 1:2 to 1:3, the aqueous sodium silicate spray droplets are of weight average diameter no greater than one millimeter, and the mixing, spraying, agglomerating and subsequent mixing take place continuously in a rotary drum type mixer.

29. A process as claimed in Claim 27 or Claim 28 in which the rotary drum type mixer extends longitudinally at an angle of from about 2 to 15° to the horizontal, the initial mixing takes place within about the upstream third of the length of the drum, the spraying takes place within about the middle third of the drum and the subsequent mixing takes place within about the downstream third of the drum, the detergent composition particles and bentonite powder are continuously added to the upstream end of the drum, the sodium silicate solution spray is delivered from a plurality of spray nozzles onto the moving mixture, and the removed agglomerated product is of a bulk density within the range of 0.3 to 0.7 g/ml.

30. A process as claimed in any one of Claims 17 to 29 in which the spray dried detergent composition particles comprise anionic synthetic organic detergent and/or nonionic synthetic organic detergent as the active deterative component, and sodium tripolyphosphate, sodium carbonate, sodium nitrilotriacetate, sodium aluminosilicate, sodium bicarbonate, sodium silicate, sodium citrate or sodium borate or

mixtures thereof, as builder(s), with the proportions thereof being within the ranges of 5 to 35% and 30 to 90% of the product, respectively.

31. A process as claimed in any one of Claims 17 to 30 in which the bentonite powder passes through a No. 325 sieve, the spray dried detergent composition beads are of particle sizes in the range of No's. 10 to 60 sieve, and comprise 15 to 30% of sodium linear dodecylbenzene sulphonate, 20 to 50% of pentasodium tripolyphosphate, 5 to 15% of sodium silicate of $\text{Na}_2\text{O}:\text{SiO}_2$ ratio of about 1:2.4, 5 to 20% of sodium carbonate, 5 to 30% of sodium sulphate and 4 to 12% of moisture, the sodium silicate spray solution is of about 4 to 6% sodium silicate content, the $\text{Na}_2\text{O}:\text{SiO}_2$ ratio of the sodium silicate is about 1:2.4, and about 3 to 6% of the sodium silicate solution is applied to the mixture of detergent composition particles and bentonite.

32. A process as claimed in any one of Claims 17 to 31 in which the bentonite is a Wyoming bentonite having a moisture content of at least 4%, the bentonite content of the fabric softening detergent composition is from 15 to 25% thereof, the moisture content of the composition is from 7 to 15%, the average diameter of the spray droplets is in the range of from 0.1 to 0.5 millimeter, the bulk density of the agglomerated particles is within the range of 0.3 to 0.5 g/ml and the average time of material in the rotary drum is from 1 to 10 minutes.

33. A process as claimed in Claim 17 substantially as specifically described herein.

34. A product whenever made by a process as claimed in any one of Claims 9 to 16.

35. A product whenever made by a process as claimed in any one of Claims 17 to 33.